Functional Materials for Wastewater Treatment

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Contributor: Zahra Tabasi, Yuming Zhao, Nadia Khan, Baiyu Zhang, Tahir Husain

Functional materials play a central role in the advancement of these technologies due to their highly tunable properties and functions.

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1. Introduction

Wastewater is predominately discharged from domestic, industrial, and public facilities. Wastewater may contain a variety of inorganic and organic pollutants, as well as microorganisms, depending on its source(s). For example, modern manufacturing and processing industries continuously release heavy metal ions, textile dyes, and other toxic chemicals to contaminate ground water and surface water. In offshore oil and gas industrial activities, oily wastewater is massively produced during oil and gas exploration, processing, treatment, and accidental oil spills. The increasing environmental impacts by wastewater in recent years have raised growing concerns globally. If not treated timely and properly, the accumulated wastewater can lead to irreversible damages to natural ecosystems and impose serious risks to human health.

Specially designed functional materials have played an important role in combating environmental pollution. Over the past few years, the technologies of wastewater treatment have been greatly advanced by the application of various functional materials. Many novel functional materials are derived from modifications of conventional organic and inorganic materials as well as sustainable biomass and natural polymers. On the other hand, nanotechnological products such as functional nanoparticles, carbon nanofibers/nanotubes, and nanoporous materials have emerged as high-performance modifiers to dramatically change the surface properties of adsorbent materials and separation devices (e.g., meshes, membranes). With these materials, pollutants in wastewater can be effectively removed from the adsorption or phase separation approach even under harsh conditions.

2. Application of Functional Materials in Wastewater Treatment

Functional materials for wastewater treatment can be fabricated based on naturally existing or synthetic sources [1]. Herein researchers' discussions of the studies in this area are made according to the functionality and chemical nature of the materials used.

2.1. Biofilm Carriers

Biofilms are one of the most commonly used materials in wastewater treatment. It acts as a biological filler in an aerated tank and wetland for the growth and adhesion of microorganisms. The biofilm itself does not effectively remove pollutants; however, it shows good resistance to the degradation caused by microorganisms, owing to its rough and durable surface. Biofilm carriers are mainly elastic fillers made from polymers or ceramsite materials such as shale, volcanic rock, and clay. Ceramsite is the most widely used biofilm carrier for wastewater treatment [1]. The shape and strength of ceramsite particles depend on manufacturing processes. In recent years, a variety of raw materials such as fly-ash, river sludge, steel slag, straw, and sewage sludge have been used as biofilm carriers. Compared with the traditional ceramsites, these new materials show better performance in biofilm growth and removal of nitrogen, phosphorous, organic matter, and heavy metals.

In 2021, Amshawee et al. [2] contributed a systematic review on the importance of biofilm carrier roughness in facilitating the growth of microorganisms by providing substratum for their attachment. It has been concluded that increased roughness enhances surface wettability to protect the microbial communities from being detached. Wang and co-workers [3] used different types of biofilm carriers, such as carbon fibers, polyurethane, or non-woven fabrics, to fabricate a fixed-bed baffled reactor for removal of nitrogen from synthetic aquaculture wastewater by means of microbial nitrification and denitrification reactions. Their work showed that carbon fibers have a great potential in aquaculture wastewater treatment, and different types of biofilm carrier materials influence the biofilm formation in different ways. Makisha et al. [4] studied five types of polymer biofilm carriers in order to achieve improvement on secondary wastewater treatment for removing organics and nutrients in an aerobic reactor. They investigated the performance of three benches filled with a floating carrier with a filling percent of 10%, 20%, and 30%, respectively. Their study showed 95–96% effective BOD (biochemical oxygen demand) removal in filling ratio benches and 92% removal in a control bench that contains no floating carriers. For ammonia nitrogen, the removal efficiency of the control bench was only 55%, while floating carriers helped to increase the efficiency up to 70–86%. The above-mentioned studies on biofilm carriers in recent years are summarized and compared in **Table 1**.

Table 1. Studies of biofilm carriers for removal of organics and nutrients in secondary treatment.

Authors (Year)	Materials Used	Outcomes
Amshawee et al. (2021)	**Biofilm carrier**	**Roughness enhances wettability and protects microbial communities from detachment.**
Wang et al. (2021)	**Carbon fibers, polyurethane, non-woven fabrics**	**Carbon fibers show more potential in aquaculture wastewater treatment.**
Makisha et al. (2021)	**Polymer biofilm carriers**	**The removal efficiency is enhanced by increasing the ratio of the floating carrier.**

2.2. Sand Filters

Sand has been for a long time used as a filter for the treatment of wastewater, drinking water, and other water purification processes. Sand is a simple and low-cost material, but lacks the capability of removing toxic and harmful substances. Currently, active research is being conducted on how to improve the performance of sand filters in terms of surface, mechanical, and adsorption properties. In 2018, Chen et al. [1] investigated quartz sand as a functional carrier. With a method of repeated heating and steaming, they prepared a type of aluminum salt-modified quartz sand, which gave an excellent performance in algae removal in comparison with unmodified quartz sand filter. Saini and co-workers [5] in 2021 designed a simple and cost-effective method for the treatment of wastewater generated by household, canteen and the laboratory of an academic institute. The study explored the removal of metal ions and phosphate ions from wastewater by using plant species, such as Typha latifolia L. and Canna indica, through the phytoremediation process. The various water quality parameters were analyzed. Their method achieved a significant reduction in hardness, turbidity, and chemical oxygen demand, as well as an increase in dissolved oxygen value. The treated water could be brought into various uses such as household works and agriculture. Very recently, Yan et al. [6] investigated the performance of superhydrophilic and superhydrophobic quartz sand filters with Janus channels in the separation of surfactant stabilized oil-in-water and water-in-oil emulsions. Based on computational and experimental studies, they concluded that the Janus channels in the mixed sand layer give better demulsification capability and separation performance, due to high interaction energy with emulsified oil droplets. The as-prepared Janus sand filter showed excellent recyclability, environmental friendliness and great potential in the separation of surfactant stabilized oil–water emulsions. **Table 2** compares the two recent studies on modified sand filters as mentioned above.

Table 2. Studies of sand filters for demulsification and separation oil/water mixtures.

Authors (Year)	Materials Used	Outcomes
Saini et al. (2021)	**Typha latifolia L. and Canna indica**	**Significant reduction in hardness, turbidity and chemical oxygen demand. Dissolved oxygen value are increased.**
Yan et al. (2021)	**Quartz sand filter with Janus channels**	**The Janus channels exhibit excellent demulsification capability and separation performance.**

2.3. Biomass Materials

Rice-husk (RH), coconut shells, and sawdust are excellent sources of biomass materials. RH is an agricultural by-product that can be used for the removal of cationic dyes (e.g., methylene blue) and crystal violet (methyl violet) from wastewater. Compared with other adsorbents, RH shows low adsorption capacity for various dyes, but its low costs and abundant availability are advantageous for large-scale industrial application; for example, removal of dyes from textile wastewater [7]. Another important application of this type of materials can be found in the production of biochar using palm kernel shell as an efficient and cost-effective adsorbent to remove dyes from wastewater [8]. An intriguing honeycomb like carbon foam was recently produced by Tan et al. [9] from larch sawdust and this material can serve as a hydrophobic adsorbent for oil spill cleanup. To make such adsorbent, liquefied-larch based polymer foam (LLB-PF) and its carbonized products were prepared. It has been found that 3D interconnected and open cell honeycomb structures still remain intact even after the carbonization process. These two ultra-light foams exhibited rapid adsorption capacity not only for oils but also for organic solvents. A comparison of these two studies of biomass materials is made in **Table 3**. It is worth noting that a comprehensive review was published by Vishnu and co-workers in 2022 [10], summarizing the application of different types of adsorbents produced from agricultural waste, activated carbons, nanomaterials, and biomaterials.

Table 3. Studies of biomass for removal of oils and dyes from wastewater.

Authors (Year)	Materials Used	Outcomes
Tan et al. (2018)	**liquefied-larch based polymer foam**	**This ultra light foam exhibits rapid adsorption capacity for oils and organic solvents.**
Quansha et al. (2015)	**Agricultural by-products (e.g., peanut husk, wheat straw)**	**Dyes can be removed by these materials.**

2.4. Chitosan-Based Biopolymers

Chitosan is a mucopolysaccharide found in the shell of crabs and shrimps (**Figure 1**), usually obtained by treating the shell with sodium hydroxide. In this reaction, the acetyl groups of the biopolymer are hydrolyzed, leading to the formation of free primary amino groups in the molecular structure of the biopolymer. Chitosan has been recognized as an alternative adsorbent for the removal of copper, chromium, and dyes from wastewater.

Figure 1. Chitosan from marine crustacean products (picture adopted from https://zenonco.io/cancer/chitosan/).

Due to the presence of free primary amino sites, the adsorption of dyes and formation of chelates with metal ions under acidic conditions can occur easily, making chitosan a suitable and cost-effective option for the adsorptive removal of various pollutants from wastewater. Chitosan is readily soluble in water, even in weakly acidic aqueous solutions. Many research works on chitosan in the past few years were focused on developing methods for reducing its solubility. Cross-linking the chitosan chains through reacting their amino sites with cross-linking agents is an effective approach for making low-solubility chitosan. On the other hand, cross-linking reduces the adsorption capability of chitosan. Using carbon tetrachloride as a cross-linking agent, Ramnani and Sabharwal [11] reported a radiation-assisted method, in which chitosan was cross-linked in a 60

Co gamma irradiation chamber. Through this treatment, the cross-linked chitosan attained a much better adsorption capacity than chemically cross-linked chitosan. Li et al. [12] in 2015 investigated a method of coating silica gel particles on chitosan. The resulting materials showed high surface areas which allow easy access to active amino sites. The modification methods and adsorptive performance of the chitosan materials in the above-mentioned studies are summarized and compared in **Table 4**. The readers are also referred to a review authored by Upadhyay et al. in 2021, which has comprehensively summarized the performance of chitosan-based adsorbents for removal of heavy metal ions [13]. Moreover, that review article has discussed the common chitosan modification methods and the design of chitosan-based adsorbents in fixed bed column packaging for industrial wastewater treatment. It has been concluded that cross-linking and grafting are the most popular methods. Chitosan-based adsorbents in column bed packaging perform much better than commercial adsorbents in the continuous flow process.

Table 4. Studies on chitosan-based functional materials for adsorptive application.

Authors (Year)	Materials Used	Outcomes
Ramnani et al. (2006)	**Carbon tetrachloride-crosslinked chitosan**	**Improved adsorption capacity, and less soluble in acid.**
Li et al. (2015)	**Silica gel particle-coated chitosan**	**Surface area and adsorption capacity are increased.**

2.5. Inorganic Materials

Functional materials based on carbon or minerals belong to the category of inorganic functional materials. Inorganic Materials can be also applied in wastewater treatment.

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